La$_5$Ti$_2$Cu$_{1-x}$Ag$_x$S$_5$O$_7$ photocathodes operating at positive potentials during photoelectrochemical hydrogen evolution under irradiation of up to 710 nm†

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A photoelectrochemical (PEC) cell based on a series-connected photocathode and photoanode made of particulate semiconductors is a potentially scalable and inexpensive device for renewable solar hydrogen production via PEC water splitting without any external power supply. The realisation of such PEC devices hinges on the development of photoelectrodes that operate at a small applied voltage. In this study, solid solutions of La$_5$Ti$_2$Cu$_y$S$_5$O$_7$ (LTC) and La$_5$Ti$_2$Ag$_y$S$_5$O$_7$ (LTA) were synthesised, and their physical, optical, and PEC properties in the water splitting reaction were discussed. LTC and LTA formed a La$_5$Ti$_2$Cu$_{1-x}$Ag$_x$S$_5$O$_7$ solid solution (LTC$_{1-x}$Ag$_x$) over the whole compositional range. The indirect bandgap energy of LTC$_{1-x}$Ag$_x$ changed nonlinearly with respect to composition, attaining its minimum value (ca. 1.8 eV) at a composition of $x \approx 0.16$. Photoelectrodes of Al-doped LTC$_{1-x}$Ag$_x$ solid solution powder fabricated using the particle transfer method exhibited a photocathodic response regardless of the Ag content. 1%Al-LTC$_{0.9}$Ag$_{0.1}$ photocathodes exhibited the best PEC properties in the hydrogen evolution reaction and yielded a hypothetical half-cell solar-to-hydrogen energy conversion efficiency of 0.25% at +0.6 V vs. RHE, three times higher than the previously reported 1%Sc-LTC. In addition, 1%Al-LTC$_{0.9}$Ag$_{0.1}$ photocathodes were fairly stable at +0.7 V vs. RHE without any protective modifications. Owing to the positive operational electrode potential of 1%Al-LTC$_{0.9}$Ag$_{0.1}$, unassisted PEC water splitting was accomplished using series-connected photoelectrodes made of 1%Al-LTC$_{0.9}$Ag$_{0.1}$ and BaTaO$_2$N, particulate semiconductors with absorption edge wavelengths of 710 and 660 nm, respectively, at a Faradaic efficiency of unity and a solar-to-hydrogen energy conversion efficiency of approximately 0.1%.

Introduction

Photoelectrochemical (PEC) water splitting has been studied extensively as a means of renewable hydrogen production from water and solar energy on a large scale.1–6 The hydrogen thus produced does not depend on fossil fuels and leaves only water...
as a by-product when used as a fuel to drive fuel cells and in a combustion process. Hydrogen is also an important feedstock for various chemicals in the chemical industry. In particular, the reduction of carbon dioxide using solar-derived hydrogen is considered to have significant impact on the energy efficiency of the process. The storage and transportation of hydrogen in the form of liquid-organic hydrides have also been studied.

A technoeconomical analysis published in 2013 suggests that the cost of hydrogen produced by PEC water splitting can be low enough to be competitive with the steam methane reforming process. However, a solar-to-hydrogen energy conversion efficiency (STH) of at least 10% is needed to realise this ideal scenario. Achieving an STH of 10% at a feasible quantum efficiency clearly requires harvesting of long-wavelength photons. In addition, the cost and scalability of PEC systems are important for practical applications. It was found that 80% of the cost of hydrogen would originate from the capital cost when panel array PEC cells based on integrated thin films are used. The development of particulate photoelectrode devices capable of decomposing water into hydrogen and oxygen without external bias can solve this problem, because photoelectrodes made of particulate semiconductors can in principle be fabricated by inexpensive and scalable printing processes.

In 2004, Meignen et al. reported La3Ti3Cu2S5O7 (LTC) and La3Ti2AgS5O7 (LTA) to be semiconducting oxysulphides with bandgap energies of 2.0 and 2.2 eV, respectively. LTC has a longer absorption edge wavelength than LTA because Cu 3d orbitals form the top of the valence band and shift the valence band maximum negatively. The present authors’ group study that the PEC properties of the LTC powder decreased due to the presence of oxide impurities. The precursor mixture of LTC was doped with Al, the amount of TiO2 was reduced and corresponding amounts of Al2O3 were added. The Al-doped La3Ti2Cu1−xAxAgS5O7 samples will hereafter be referred to as Al-LTC1−xAx.

### Experimental

LTC1−xA solid solution powders were synthesised by solid state reactions in sealed evacuated tubes. La2O3 (99.99%, Kanto Chemical Co., Inc.), freshly calcined at 1273 K for 10 h, La2S3 (99.9%, Kojundo Chemical Laboratory Co., Ltd), TiO2 (99.99%, Rare Metallic Co., Ltd), freshly calcined at 1073 K for 1 h, Cu2S (99%, Kojundo Chemical Laboratory Co., Ltd), Ag2S (99%, Kojundo Chemical Laboratory Co., Ltd), Al2O3 (99.99%, 0.3 μm, Sodeka Chemicals), freshly calcined at 1273 K for 6 h, and S (99.99%, Kojundo Chemical Laboratory Co., Ltd) were stored and used as raw materials in a glovebox under a nitrogen atmosphere. La2O3, La2S3, TiO2, Cu2S, Ag2S, and S were mixed in the glovebox at a molar ratio of 2:3:4:1 − x:0.25. Here, sulphur was added excessively to suppress the generation of oxide impurities. It was found in our previous study that the PEC properties of the LTC powder decreased due to the presence of oxide impurities. The precursor mixture was sealed in evacuated quartz tubes and heated at 1273 K for 48 h. After heating, the samples were ground into powder. When LTC1−xA was doped with Al, the amount of TiO2 was reduced and corresponding amounts of Al2O3 were added. The Al-doped La3Ti2Cu1−xAxAgS5O7 samples will hereafter be referred to as Al-LTC1−xAx.
X-ray diffraction (XRD) patterns were acquired using an X-ray diffractometer (RINT-Ultima-III, RIGAKU). The crystal structure was depicted using the VESTA software package\textsuperscript{,28} and the crystallographic information files for LTC and LTA.\textsuperscript{11} Diffuse reflectance spectra (DRS) were recorded using an ultraviolet-visible-infrared diffuse reflectance spectrometer (V-670, JASCO). The indirect bandgap energy was estimated from the following equation:

\[
(\text{zhv})^n = A(hv - E_g)
\]

where \(z\) is the absorption coefficient, \(hv\) is the photon energy, \(A\) is a proportionality constant, \(E_g\) is the bandgap energy for a semiconductor, and \(n\) is 0.5 for indirect allowed transitions. The Kubelka–Munk function was used as the absorption coefficient, assuming that the scattering coefficient was unchanged near the absorption edge. The morphology of the LTC_{\text{1-x}}A\text{_x} particles on a photoelectrode was observed using field-emission scanning electron microscopy (FE-SEM, Hitachi, S-4700 and SU-8020).

Photoelectrodes of LTC_{\text{1-x}}A\text{_x} were prepared using the particle transfer method.\textsuperscript{14,29} A Au layer thicker than 2 \(\mu\)m was deposited by vacuum evaporation on LTC_{\text{1-x}}A\text{_x} powder piled on a glass plate. Then, carbon tape supported by a glass plate was used to peel off the Au layer and LTC_{\text{1-x}}A\text{_x} powder composite from the original glass plate. Excess particles were removed by sonication. LTC_{\text{1-x}}A\text{_x} photoelectrodes consisted of only a few layers of particles as shown in Fig. S1 in the ESI.\textsuperscript{†} Accordingly, the thickness of the LTC_{\text{1-x}}A\text{_x} particle layer was a few micrometres at most. This is in fact key to minimize the number of grain boundaries and ensure adequate mechanical and electric contacts between LTC_{\text{1-x}}A\text{_x} particles and the underlying Au conductive layer. An electric wire was soldered to the electrode and covered with epoxy resin. Pt was deposited on the LTC_{\text{1-x}}A\text{_x} photoelectrodes by potentiostatic photodeposition under simulated sunlight (AM1.5G, SAN-EI Electric Co., Ltd, XES-4052-CE) in an aqueous solution (100 mL) of Na\textsubscript{2}SO\textsubscript{4} (0.1 M), K\textsubscript{2}C\textsubscript{2}O\textsubscript{4} (0.1 M), and H\textsubscript{2}PtCl\textsubscript{6} (3.5 \(\times\) 10\textsuperscript{-6} M).\textsuperscript{15} A Ag/AgCl electrode and Pt wire were used as reference and counter electrodes, respectively. The pH of the electrolyte solution was adjusted to 10 by an aqueous NaOH solution. During the photodeposition reaction, the electrolyte solution was stirred while bubbling Ar.

The current–potential curves were measured using a three-electrode system with Ag/AgCl and Pt electrodes as reference and counter electrodes, respectively. A 0.1–0.5 M Na\textsubscript{2}SO\textsubscript{4} solution (100 mL) was used as electrolyte solution. The pH of this solution was adjusted to 10 by an aqueous NaOH solution (0.1 M). A solar simulator was used as a light source. The potential of the electrode was controlled by an automatic polarization system (Hokutodenko, HSV-110). The incident photon-to-current efficiency (IPCE) was measured at 0 and +0.65 V vs. RHE under a 300 W Xe lamp (MAX-302, Asahi Spectra) equipped with a series of band-pass filters.

A p/n PEC cell was prepared by connecting Pt-loaded AL-LTC_{\text{0.9A\textsubscript{0.1}}} (Pt/AL-LTC_{\text{0.9A\textsubscript{0.1}}}) and cobalt-species-loaded BaTaO\textsubscript{2}N (Co/BaTaO\textsubscript{2}N) photoelectrodes\textsuperscript{27} fabricated separately. The photoelectrodes were mounted side by side on a glass plate. The pH of the aqueous Na\textsubscript{2}SO\textsubscript{4} solution (0.1 M) used as the electrolyte solution was adjusted to 11 with an aqueous NaOH solution (5 M). A p/n PEC cell of Pt/LTC_{\text{0.9A\textsubscript{0.1}}} and Co/BaTaO\textsubscript{2}N was immersed in the electrolyte solution in an airtight reactor with a flat window and a cooling jacket. The reactor was purged with Ar and maintained at atmospheric pressure. The p/n PEC cell was irradiated with visible light from a 300 W Xe lamp through a cutoff filter (\(\lambda \geq 420\) nm) or the simulated sunlight. During the measurement, the photocurrent and the electrode potential were monitored using two automatic polarization systems: one was used for chronopotentiometry in the two-electrode configuration with no applied voltage to record the photocurrent passing between the Pt/LTC_{\text{0.9A\textsubscript{0.1}}} and Co/BaTaO\textsubscript{2}N photoelectrodes, and the other was used for measuring the rest potential to record the electrode potential of the p/n PEC cell vs. a Ag/AgCl reference electrode. The electrode potential of the p/n PEC cell was equal to those of the Pt/LTC_{\text{0.9A\textsubscript{0.1}}} and Co/BaTaO\textsubscript{2}N photoelectrodes. The amounts of H\textsubscript{2} and O\textsubscript{2} evolved were quantified using an on-line micro-gas chromatograph (3000A, Agilent).

**Results and discussion**

Fig. 1 and 2 show the XRD patterns and the lattice spacing for the (714) diffraction of LTC_{\text{1-x}}A\text{_x} prepared by a solid state reaction. Fig. 1 also shows the simulated XRD patterns for LTC and LTA, available in the Inorganic Crystal Structure Database (ICSD), as a reference.\textsuperscript{11} LTC and LTA were obtained as the major phases at compositions of \(x = 0\) and 1.0, respectively, similarly to our previous work.\textsuperscript{12} The XRD patterns for LTC_{\text{1-x}}A\text{_x} with varying compositions were similar to those for LTC and LTA, but shifted to lower angles with increasing Ag content.
This reflects the fact that the Ag\(^+\) ion has a larger ionic radius than the Cu\(^+\) ion. The dependence of the lattice spacing of the (714) planes on the composition could be approximated linearly by following Vegard’s law. These observations indicated that \(\text{LTC} 1_{\text{x}}\text{A}_{\text{x}}\) was not a physical mixture of \(\text{LTC}\) and \(\text{LTA}\), but rather formed a solid solution over the whole composition range. The lattice constants of \(\text{LTC}\) and \(\text{LTA}\) differ by less than 1%. Therefore, they can form a solid solution. Likewise, Al-doped \(\text{LTC} 1_{\text{x}}\text{A}_{\text{x}}\) formed a solid solution. As shown in Fig. S2 in the ESI, the diffraction patterns were attributed to the \(\text{LTC}\) and \(\text{LTA}\) structures, and the lattice spacing of the (714) planes was fitted with a straight line over the whole composition range.

Fig. 3 shows the DRS of \(\text{LTC} 1_{\text{x}}\text{A}_{\text{x}}\) solid solutions. The onset values for light absorption by \(\text{LTC}\) and \(\text{LTA}\) from the background absorption were comparable to those obtained in our previous study.\(^{12}\) Substituting Ag for 10% of the Cu shifted the absorption edge toward longer wavelengths. However, further substitution shortened the absorption edge wavelength. As a consequence, \(\text{LTC}\) and \(\text{LTC} 0.7\text{A}0.3\) exhibited virtually the same absorption edge wavelength. The dependence of the optical properties of \(\text{LTC} 1_{\text{x}}\text{A}_{\text{x}}\) solid solutions on the Ag content can be plainly observed by comparing the indirect bandgap energies, as shown in Fig. 4. Clearly, the bandgap energy exhibited a nonlinear dependence on the composition of the \(\text{LTC} 1_{\text{x}}\text{A}_{\text{x}}\) solid solution. Some solid solution semiconductors, such as \((\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)\),\(^{30–32}\) \(\text{Al}_{1-x}\text{In}_x\text{N}\),\(^{33}\) and \(\text{Ag}_{\text{x}}\text{Gu}_{1-x}\text{GaSe}_2\),\(^{34}\) are known to behave similarly. The bandgap energies of solid solutions of semiconductors \(\text{A}\) and \(\text{B}\) \((\text{A}_{1-x}\text{B}_x)\) can be empirically expressed in the following manner:

\[
E_{\text{g,AB}} = xE_{\text{g,A}} + (1 - x)E_{\text{g,B}} - bx(1 - x)
\]

\[
= bx^2 + (E_{\text{g,A}} + E_{\text{g,B}} - b)x + E_{\text{g,A}} + E_{\text{g,B}},
\]

where \(E_{\text{g,AB}}, E_{\text{g,A}},\) and \(E_{\text{g,B}}\) are the bandgap energies of semiconductors \(\text{A}_{1-x}\text{B}_x\), \(\text{A}\), and \(\text{B}\), respectively, and \(b\) is the bowing parameter. \(\text{LTC} 1_{\text{x}}\text{A}_{\text{x}}\) solid solutions had a bowing parameter of 0.62 eV and the narrowest bandgap energy at a composition of \(x \approx 0.16\). The indirect bandgaps of the solid solutions 1%\text{Al-LTC}1_{\text{x}}\text{A}_{\text{x}}\) and 2%\text{Al-LTC}1_{\text{x}}\text{A}_{\text{x}}\) showed a nonlinear composition dependence with bowing parameters of 0.57 and 0.60 eV, respectively, as seen in Fig. S3 and S4 in the ESI.\(^{†}\)

On the basis of the outcome of density functional theory (DFT) calculations in our previous study,\(^{12}\) it is thought that the valence and conduction bands of \(\text{LTC} 1_{\text{x}}\text{A}_{\text{x}}\) are spatially localised around one-dimensional chains of \((\text{Cu}_{1-x}\text{Ag}_x)\)\text{S}_4\) tetrahedra and \(\text{Ti}(\text{O,S})_6\) octahedra, respectively. \(\text{LTC}\) has a narrower...
bandgap energy than LTA because Cu 3d orbitals with a more negative potential than S 3p and O 2p make a major contribution to the valence band edge of LTC. Therefore, LTC$_{1-x}$A$_x$ with $x \approx 0.16$ would not be expected to have a narrower bandgap energy than LTC and LTA. Rather, this can be explained by the density of the Cu 3d orbitals and the lattice constants of the LTC$_{1-x}$A$_x$ solid solution system. The density of states and the width of a band consisting of Cu 3d orbitals become fewer and thinner with decreasing Cu content. Because the valence band edge of LTC$_{1-x}$A$_x$ is not due to the local inhomogeneity of the solid solution, because LTC$_{1-x}$A$_x$ can have a narrower bandgap energy than LTC and LTA. Rather, this can be explained by the density of the Cu 3d orbitals and the lattice constants of the LTC$_{1-x}$A$_x$ solid solution system. The density of states and the width of a band consisting of Cu 3d orbitals become fewer and thinner with decreasing Cu content. Because the valence band edge of LTC$_{1-x}$A$_x$ is composed mainly of Cu 3d orbitals, the decrease in Cu content will shift the valence band edge of LTC$_{1-x}$A$_x$ positively and increase the bandgap energy. On the other hand, it is empirically known that for most solid solutions of metal pnictogenide or chalcogenide semiconductors, the bandgap energy decreases as the lattice constant increases. The lattice constants of LTC$_{1-x}$A$_x$ increased linearly with increasing Ag content (Fig. 2), reflecting the larger lattice constants of LTA as compared to those of LTC. These two factors affect the bandgap energy of LTC$_{1-x}$A$_x$ in opposite ways. As a result, the bandgap energy of LTC$_{1-x}$A$_x$ may show a nonlinear dependence on composition. Structural optimisation and band structure calculations are in progress for a more conclusive discussion.

PEC properties of LTC$_{0.9A_{0.1}}$ photoelectrodes with different Al doping amounts were studied by taking into account their longer absorption edge wavelengths as compared to those of LTC and LTA. Fig. 5 shows the current–potential curves measured under simulated sunlight in an aqueous solution of Na$_2$SO$_4$ solution at pH 10. The LTC$_{0.9A_{0.1}}$ photoelectrodes functioned as photocathodes and generated a photocathodic current regardless of whether they were Al doped or not. The photocathodic current increased significantly upon Al doping, particularly in the positive potential regions near the onset of the photocathodic current. This is consistent with our previous study on LTC in that doping lower-valence cations in the Ti$^{4+}$ sites enhanced the photocathodic response most likely because of an increase in the majority carrier concentration. However, excessive doping (2%) weakened the enhancement presumably because of the formation of defect species. Transient photocurrent spikes owing to charging and discharging of surface states were observed near the onset potential of the photocathodic current. Similarly to previously reported LTC photocathodes, 1%Al-LTC$_{0.9A_{0.1}}$ generated a photocathodic current at 0.8–0.9 V vs. RHE, which is markedly positive compared to many other single semiconductor photocathode materials. The onset potential is positive enough to construct p/n PEC cells in combination with existing sunlight-driven photoanodes such as BiVO$_4$, Ta$_3$N$_5$, and BaTaO$_2$N without photovoltaic assistance. The photocathodic current increased as the electrode potential became more negative. The hypothetical half-cell solar-to-hydrogen energy conversion efficiency (HC-STH) peaked at +0.6 V vs. RHE and was estimated to be 0.25%, which represents a threefold improvement over that for Sc-LTC. HC-STH is lower than existing state-of-the-art photocathodes, such as planar and nanorod-type Si$^{18}$ and Cu(In,Ga)Se$_2$-based thin films. However, it should be noted that the optimum operational positive potential is unique to 1%Al-LTC$_{0.9A_{0.1}}$ and suitable for the construction of p/n PEC cells.
The durability of 1%Al-LTC\textsubscript{0.9A0.1} photocathodes in the positive potential region was examined. Fig. 6 shows a typical current–time profile for a 1%Al-LTC\textsubscript{0.9A0.1} photocathode measured at +0.7 V vs. RHE. In the initial hour, the photocurrent was decreased by approximately 40%. The photocurrent became relatively stable in the following measurement, maintaining a photocathodic current of 0.12 mA cm\textsuperscript{-2} after 16 h of illumination. Fig. S5 (ESI\textsuperscript{†}) shows SEM images of 1%Al-LTC\textsubscript{0.9A0.1} photoelectrodes before and after a 1.5 hour potentiostatic PEC hydrogen evolution reaction at +0.7 V vs. RHE. Rod-like particles of 1%Al-LTC\textsubscript{0.9A0.1} were observed before and after the PEC measurement. Neither a significant loss of 1%Al-LTC\textsubscript{0.9A0.1} particles nor a change in morphology because of segregation of reduced Cu or Ag typical of unprotected Cu\textsubscript{2}O photocathodes was detected.\textsuperscript{37} Thus, the photoelectrode was mechanically and chemically stable at this timescale and under these experimental conditions. 1%Al-LTC\textsubscript{0.9A0.1} is a rare photocathode material that can maintain a photocathodic response at a potential as positive as +0.7 V vs. RHE without any protecting modifications. In our preliminary experiments, the stability of the 1%Al-LTC\textsubscript{0.9A0.1} photocathode was sensitive to the kinds of ionic species present in the reaction solution. This suggests that the decrease in photocurrent might be attributable in part to the adsorption of specific ionic species. It is believed that the use of appropriate surface modifications and supporting electrolytes improves the stability of 1%Al-LTC\textsubscript{0.9A0.1} photocathodes.

Fig. 7 shows the dependence of the photocathodic current for 1%Al-LTC\textsubscript{1-xA_x} photoelectrodes at 0 and +0.6 V vs. RHE under simulated sunlight irradiation in an aqueous Na\textsubscript{2}SO\textsubscript{4} solution at pH 10. 1%Al-doped LTC\textsubscript{1-xA_x} photoelectrodes functioned as photocathodes and generated a photocathodic current regardless of the composition. The photocathodic current for 1%Al-LTC was significantly increased by substituting Ag for 10% of the Cu. Further substitution decreased the photocathodic current. The photocathodic response of 1%Al-LTA was rather weak despite the ability to absorb sunlight up to ca. 550 nm and the high hydrogen evolution activity of the LTA powder suspension. It is known that for some Cu-based chalcogenide semiconductors, the replacement of Cu with Ag tends to weaken the p-type semiconducting character or even convert these p-type semiconductors into n-type semiconductors.\textsuperscript{34} Similarly, Al-LTA may almost lose its functionality as a photocathode.

To discuss the cause of the increase in the photocathodic current upon the replacement of 10% of Cu with Ag in LTC, IPCE spectra of 1%Al-LTC\textsubscript{0.9A0.1} and 1%Al-LTC were recorded (Fig. 8). As a general trend, the IPCE increased as the illumination wavelength decreased and the electrode potential became more negative because of the shorter light penetration depth and the wider depletion layer. Both of these trends enabled more efficient electron collection at surface active sites. 1%Al-LTC\textsubscript{0.9A0.1} showed an appreciable photoresponse under illumination of up to 710 nm at 0 and +0.6 V vs. RHE while 1%Al-LTC did not. This result agreed well with the light absorption properties of these two materials (Fig. S2, ESI\textsuperscript{†}): 1%Al-LTC\textsubscript{0.9A0.1} has a narrower bandgap energy than 1%Al-LTC. In addition, the IPCE of 1%Al-LTC\textsubscript{0.9A0.1} was higher than that of 1%Al-LTC over the whole wavelength region measured. This suggests that charge separation and migration in 1%Al-LTC\textsubscript{0.9A0.1} particles were more efficient than in 1%Al-LTC. The band distribution and effective masses of charge carriers will be evaluated by DFT.
calculation to reveal the behaviour of photoexcited carriers in LTC$_{1-x}$A$_x$ solid solutions.

Given that 1%Al-LTC$_{0.9}$A$_{0.1}$ is capable of generating an appreciable photocathodic current at +0.7 V vs. RHE, unassisted PEC water splitting is feasible using a 1%Al-LTC$_{0.9}$A$_{0.1}$ photocathode and a photoanode with a photoanodic current onset potential more negative than +0.7 V vs. RHE. In this study, 1%Al-LTC$_{0.9}$A$_{0.1}$ and BaTaO$_2$N photoelectrodes were used as the photocathode and photoanode of a p/n PEC cell for unassisted water splitting because of their ability to absorb visible light up to 710 and 660 nm, respectively. The details of the preparation and the PEC properties of BaTaO$_2$N photoanodes were reported elsewhere. Fig. 9 shows the time course of the gas evolution on a p/n PEC cell of Pt/Al-LTC$_{0.9}$A$_{0.1}$ (0.43 cm$^2$) and Co/BaTaO$_2$N (2.32 cm$^2$) placed side by side. The electrolyte used was a 0.1 M aqueous Na$_2$SO$_4$ solution whose pH was adjusted to 11.

Fig. 9 Unassisted PEC water splitting under visible light irradiation from a 300 W Xe lamp ($\lambda > 420$ nm) by a p/n PEC cell consisting of Pt/Al-LTC$_{0.9}$A$_{0.1}$ (0.43 cm$^2$) and Co/BaTaO$_2$N (2.32 cm$^2$) placed side by side.

Conclusions

Solid solutions of LTC and LTA doped with Al were prepared and their structural, optical, and PEC properties in the water splitting reaction were studied. XRD analysis revealed that LTC and LTA formed LTC$_{1-x}$A$_x$ solid solutions over the whole compositional range (0 $\leq$ x $\leq$ 1). The lattice spacing of LTC$_{1-x}$A$_x$ solid solutions changed linearly with respect to the Ag content. It was found that the indirect bandgap energy depended on the Ag content with a bowing parameter of approximately 0.6 eV and was minimised at x $\approx$ 0.16. The LTC$_{1-x}$A$_x$ photoelectrodes functioned as photocathodes in the PEC water splitting reaction. The PEC properties in the hydrogen evolution reaction were significantly enhanced by Al doping, peaking at a composition of 1%Al-LTC$_{0.9}$A$_{0.1}$. Incorporation of Ag into Al-LTC not only extended the wavelength region in which the photocathode functioned to ca. 710 nm, but it also increased the IPCE at the respective wavelengths, which points to an improvement in the carrier separation and transport properties of the semiconducting powder. 1%Al-LTC$_{0.9}$A$_{0.1}$ exhibited a HC-STH of 0.25% at +0.6 V vs. RHE and generated a photocathodic current over 16 h at +0.7 V vs. RHE. This characteristic functionality as a photocathode enabled a p/n PEC cell of 1%Al-LTC$_{0.9}$A$_{0.1}$ and BaTaO$_2$N to accomplish unassisted PEC water splitting using only particulate semiconductors with PEC activity under an irradiation of up to 710 and 660 nm, respectively. The emergence of 1%Al-LTC$_{0.9}$A$_{0.1}$, characterised by an outstanding positive onset potential, a Faradaic efficiency of unity during
hydrogen evolution, reasonable stability under operating conditions, and an absorption edge wavelength of 710 nm, establishes an important milestone in the development of potentially-scalable PEC systems and broadens the prospects for PEC solar water splitting technology.

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Notes and references

38 S. W. Boettcher, E. L. Warren, M. C. Putnam, E. A. Santori, D. Turner-Evans, M. D. Kelzenberg, M. G. Walter, J. R. McKone,


